

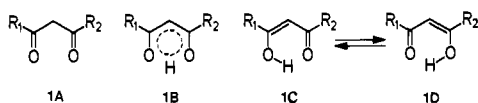
The Electronic Structure of β -Thioxoketones. A Photoelectron Spectroscopic Study of the Enol-Enethiol Tautomerism of Thioacetylacetone and Related Compounds¹

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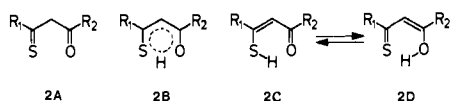
Abstract: The He I photoelectron spectra of thioacetylacetone, 2-acetylcyclohexanethione, 2-thioacetylcyclohexanone, and the *S*-methyl derivative of thioacetylacetone has been recorded and interpreted by comparison with PE data on related compounds. The interpretation has been supported by semiempirical molecular orbital calculations based on the CNDO/B, CNDO/S, and MNDO methods on the enol and enethiol forms of monothiomalondialdehyde. The three lowest ionization energies were determined as $n_s \approx \pi_3 < \pi_2$ for the enol form and as $\pi_3 < n_o < \pi_2$ for the enethiol form. The influence of hydrogen bonding on the electronic structure is discussed. Attention is called to the possibility of distinguishing generally by means of PE spectroscopy between the enol and enethiol forms of a tautomeric equilibrium system under consideration.

A major problem in recent years has been to determine the structure of the intramolecularly hydrogen-bonded enolic form of β -dicarbonyl compounds **1**.² The enolic form may be repre-



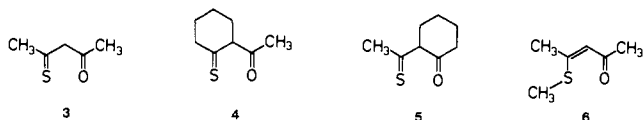
sented either by an electron-delocalized structure (**1B**) or by an equilibrium system of two rapidly interconverting enolic structures (**1C** \rightleftharpoons **1D**). Recent experimental and theoretical investigations strongly suggest that the enolic form actually exists as the **1C** \rightleftharpoons **1D** equilibrium system.³⁻⁶

Replacement of one of the β -diketone oxygen atoms by a sulfur atom leads to β -thioxoketones **2**.^{7,8} β -Thioxoketones that are not



unsuitably substituted in the α -position are known to exist as rapidly interconverting, equilibrated tautomeric forms **2C** and **2D**.⁹⁻¹¹

This paper reports on the photoelectron (PE) spectra of thioacetylacetone (**3**), 2-acetylcyclohexanethione (**4**), and 2-thio-



acetylcyclohexanone (**5**) since these compounds represent β -thioxoketones with comparable concentrations of both the enethiol and enol forms (**3**),¹⁰ with predominant concentration of the enethiol form (**4**),¹¹ and with predominant concentration of the enol form (**5**),¹¹ respectively. Supplementary, we report the PE spectrum of 4-(methylthio)pent-3-en-2-one (the *S*-methyl derivative of thioacetylacetone) (**6**) existing exclusively in the "enethiolic" form.¹⁰ The interpretation of the PE spectra is based on comparisons with PE data of related compounds and the application of Koopmans' theorem.^{12,13} The assignments have been supported by semiempirical molecular orbital calculations based on the CNDO/B,¹⁴ CNDO/S,¹⁵ and MNDO¹⁶ methods.

Experimental Section

The syntheses of the compounds **3-6** have been described previously.^{10,11} Purities were checked by ¹H NMR spectroscopy before recording

Chart I

	S=CH-CH=CH-OH	HS-CH=CH-CH=O
π_3	+ + - - +	+ - - + +
π_2	+ + + + -	+ + + - -
π_1	+ + + + +	+ + + + +

the PE spectra. The PE spectra were recorded on a PS-18 spectrometer (Perkin-Elmer) with a He I source and calibrated with a mixture of argon and xenon introduced into the target chamber simultaneously with the sample. For all compounds the spectra were recorded at room temperature. The experimental resolution was 25-35 meV. The reported ionization energies are averages of four determinations.

Qualitative Molecular Orbital Considerations

The enol as well as the enethiol form of β -thioxoketones are effectively planar molecules with intramolecular hydrogen bonds.^{9-11,17} For the parent compound, monothiomalondialdehyde, the π orbitals of the enol form, S=CH-CH=CH-OH, can be derived as combinations of the π_{C-S} , $\pi_{C=C}$, and O_{2p} fragments.¹⁸ With use of the ionization energies of the simplest substances in which these orbitals are present,¹⁹ the signs for the

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- (3) R. S. Brown, A. Tse, T. Nakashima, and R. C. Haddon, *J. Am. Chem. Soc.*, **101**, 3157 (1979) and references therein.
- (4) G. W. Mines and H. Thompson, *Proc. R. Soc. London, Ser. A*, **342**, 327 (1975).
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- (6) R. S. Brown, *J. Am. Chem. Soc.*, **99**, 5497 (1977).
- (7) The β -thioxoketones are named as such for simplicity, regardless of which of the possible tautomeric forms is dominant.
- (8) For a recent review see F. Duus (D. N. Jones, Vol. Ed.) in "Comprehensive Organic Chemistry", Vol. 3, D. H. R. Barton and W. D. Ollis, Eds., Pergamon Press, Oxford, 1979, Chapter 11.22.
- (9) L. Carlsen and F. Duus, *J. Am. Chem. Soc.*, **100**, 281 (1978).
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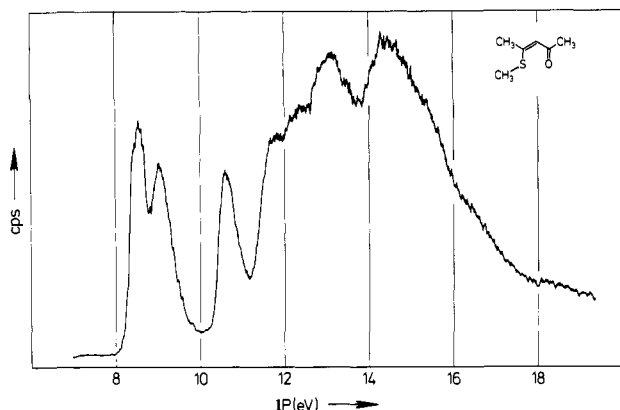


Figure 1. Photoelectron spectrum of 4-(methylthio)pent-3-en-2-one (6).

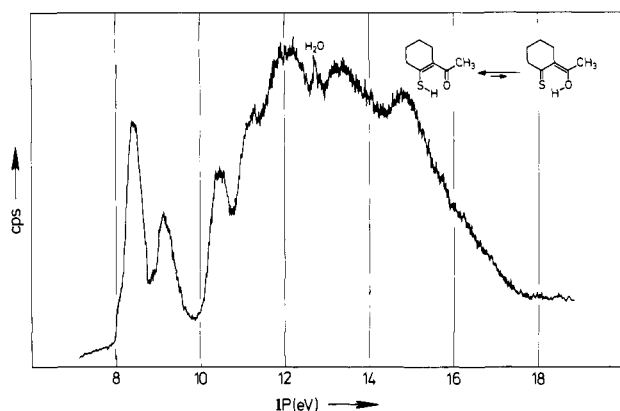


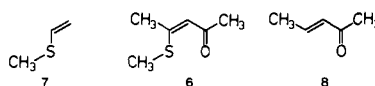
Figure 2. Photoelectron spectrum of 2-acetylcyclohexanethione (4).

three possible combinations can be outlined (Chart I). A similar qualitative orbital picture can be outlined analogously for the enethiol form, $\text{HS}-\text{CH}=\text{CH}-\text{CH}=\text{O}$ (Chart I).²² Additional low-energy orbitals of the enol and enethiol systems are the n_S and n_O lone-pair orbitals, respectively, which are orthogonal to the π orbitals mentioned above.

Photoelectron Spectra of β -Thioxoketones

The PE spectra of the β -thioxoketones 3, 4, and 5 as well as the *S*-methyl derivative 6 are depicted in Figures 1–4.

The PE spectrum of *S*-methylated thioacetylacetone 6 contains three well-resolved bands below 11 eV with maxima at 8.54, 9.03, and 10.57 eV (Figure 1). The corrected areas are nearly identical, reflecting undoubtedly single ionizations.^{21,23} The highest lying π orbital in methyl vinyl sulfide 7, mainly localized on the sulfur



atom, has been observed at 8.45 eV,^{24,25} for which reason we assign the 8.54-eV ionization as arising from a π -type orbital, π_3 (cf. Chart I). The second π orbital in methyl vinyl sulfide 7, mainly $\pi_{\text{C}=\text{C}}$, appears at 11.00 eV.^{24,25} An extension of the molecular framework with a carbonyl group (i.e., 7 \rightarrow 6) will reduce this

(19) The basis values are as follows: thioformaldehyde, $n_S = 9.33$ eV, $\pi_{\text{C}=\text{S}} = 11.90$ eV;²⁰ ethylene, $\pi_{\text{C}=\text{C}} = 10.51$ eV;²¹ water, $O_{2p} = 12.61$ eV.²¹

(20) C. Guimon, D. Gonbeau, G. Pfister-Goillouzo, L. Åsbrink, and J. Sandström, *J. Electron Spectrosc. Relat. Phenom.*, **4**, 49 (1974).

(21) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy", Wiley-Interscience, London, 1970.

(22) The basis values are as follows: formaldehyde, $n_O = 10.88$ eV, $\pi_{\text{C}=\text{O}} = 14.09$ eV;²¹ ethylene, $\pi_{\text{C}=\text{C}} = 10.51$ eV;²¹ hydrogen sulfide, $S_{3p} = 10.48$ eV.

(23) P. A. Cox and A. F. Orchard, *Chem. Phys. Lett.*, **7**, 273 (1970); P. A. Cox, S. Evans, and A. F. Orchard, *ibid.*, **13**, 386 (1972). See also ref 13, pp 38–43.

(24) H. Bock, G. Wagner, K. Wittel, J. Sauer, and D. Seebach, *Chem. Ber.*, **107**, 1869 (1974).

(25) C. Müller, W. Schäffer, A. Schweig, N. Thon, and H. Vermeer, *J. Am. Chem. Soc.*, **98**, 5440 (1976).

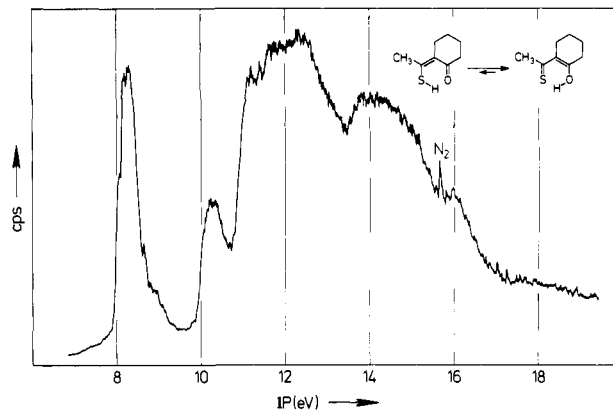


Figure 3. Photoelectron spectrum of 2-thioacetylcyclohexanone (5).

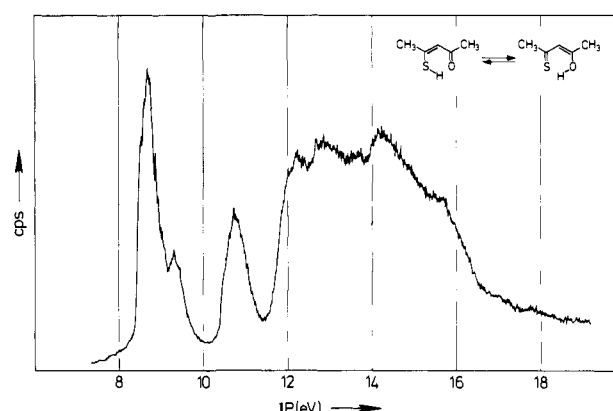
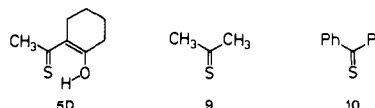


Figure 4. Photoelectron spectrum of thioacetylacetone (3).

value. In 3-penten-2-one (8) a value of 9.90 eV has been attributed to the $\pi_{\text{C}=\text{C}}$ orbital.⁴ Introduction of an *S*-methyl group (i.e., 8 \rightarrow 6) will stabilize this orbital due to interaction with the S_{3p} lone pair. Hence, it is reasonable to associate the ionization of 10.57 eV with the π_2 orbital (cf. Chart I). Consequently, the remaining ionization at 9.03 eV is assigned to the n_O orbital. The corresponding orbital in the ketone 8 is reported at 9.27 eV.⁴

In 2-acetylcyclohexanethione 4 the enol–enethiol equilibrium is shifted strongly in favor of the enethiol form 4C.¹¹ The PE spectrum of 4 (Figure 2) exhibits three low-energy ionizations at 8.34, 9.16, and 10.34 eV. These values can analogously be assigned to the π_3 , n_O , and π_2 orbitals, respectively. The destabilization of the π_3 (0.19 eV) and π_2 (0.20 eV) levels are due to the extension of the carbon framework,²⁶ whereas the replacement of the *S*-methyl group by a SH group effects a stabilization of the n_O level (0.26 eV).²⁷

In contrast to the former compound, 2-thioacetylcyclohexanone (5) exists predominantly as the enol form 5D.¹¹ The PE spectrum



of 5 (Figure 3) displays only two bands below the σ onset. The relative intensities of the bands suggest that one of these corresponds to two ionizations and the other to a single one.^{21,23} The

(26) P. Masclet, D. Grosjean, G. Mouvier, and J. Dubois, *J. Electron Spectrosc. Relat. Phenom.*, **2**, 225 (1973).

(27) The effect of methyl group replacement may be illustrated by the ionization energies of the S_{3p} lone pair through the series Me_2S (8.68 eV)²⁸ \rightarrow MeSH (9.41 eV)²⁸ \rightarrow H_2S (10.48 eV)²¹ and of the n_S lone pair in $\text{Me}_2\text{C}=\text{S}$ (8.60 eV)²⁹ \rightarrow $\text{MeHC}=\text{S}$ (8.98 eV)²⁹ \rightarrow $\text{H}_2\text{C}=\text{S}$ (9.38 eV).²⁰

(28) H. Bock and G. Wagner, *Angew. Chem.*, **84**, 119 (1972); *Angew. Chem., Int. Ed. Engl.*, **11**, 150 (1972).

(29) H. W. Kroto, B. M. Landsberg, R. J. Suffolk, and A. Vodden, *Chem. Phys. Lett.*, **29**, 265 (1974).

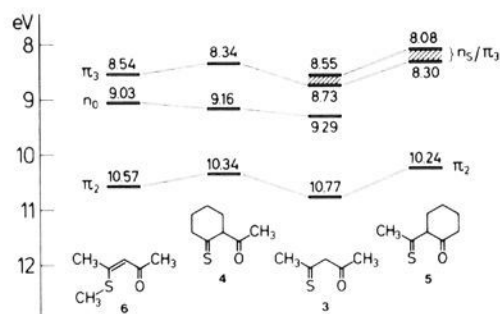


Figure 5. Energy level correlation diagram for β -thioxoketones assuming the validity of Koopmans' theorem. The numerical values refer to the experimentally determined PES ionization energies (eV, cf. Figures 1–4).

maximum of the first peak is located at 8.30 eV, exhibiting a shoulder on the low-energy side approximately at 8.08 eV, whereas the maximum of the second peak appears at 10.24 eV.

Unfortunately thiocarbonyl compounds have been investigated only sparsely by PE spectroscopy.³⁰ Nevertheless the assignment of the PE spectrum of **5** can be made adopting the ionization energies of thioacetone and thiobenzophenone as basis values. In thioacetone **9** the sulfur lone pair (n_S) and the $\pi_{C=S}$ orbitals have been reported at 8.60 and 10.46 eV, respectively.²⁹ Replacement of the methyl groups by phenyl groups (affording thiobenzophenone **10**) effects destabilization of both the n_S and $\pi_{C=S}$ orbitals.³¹ The n_S ionization energy of **5D** is a priori expected to be found between those of **9** and **10**, observed at 8.60²⁹ and 8.00 eV,³¹ respectively. The $\pi_{C=S}$ ionization energy of **5D**, on the other hand, may be expected equal or lower than those of both **9** and **10** (10.46²⁹ and 8.77 eV,³¹ respectively). Hence, the values observed at 8.08 and 8.30 eV are to be assigned to ionizations from the n_S and π_3 ($\pi_{C=S}$) orbitals, although it is impossible to distinguish between them. The lower peak at 10.24 eV is attributable to ionization from the π_2 orbital, which has mainly $\pi_{C=C}$ character.

Since PE spectroscopy is a "fast" technique, the recorded spectrum will be a superposition of the spectra of all individual species present.³² In the PE spectrum of **5** (Figure 3) the minor signal in the region about 9 eV arises presumably from the n_0 level of the minor tautomer, the enethiol **5C**.¹¹ In the case of **4** (Figure 2) a shoulder observed on the low-energy side of the first band (~ 8 eV) suggests the presence of minor quantities of the enol form **4D**¹¹ (the n_S and π_3 levels).

For thioacetylacetone **3** the enol form is the dominating tautomer, but the enethiol form is present to a comparable extent.³³ Therefore, the PE spectrum of **3** (Figure 4) must visualize ionizations arising from both tautomers. On the basis of the above findings the PE spectrum of **3** is easily interpreted (Figure 5).

The PE spectrum of **3** (Figure 4) contains three bands as expected. The band at 8.73 eV and the shoulder at 8.55 eV correspond to the π_3 orbital of the enethiol form **3C**, and the n_S and π_3 orbitals of the enol form **3D**. The band at 9.29 eV arises from ionization from the n_0 orbital of the enethiol tautomer **3C**. The third band at 10.77 eV, accompanied by a shoulder (~ 10.5 eV), corresponds to ionizations from the π_2 orbitals of both tautomers.

Molecular Orbital Calculations

In order to gain further insight into the electronic dissimilarities of the enol and enethiol forms of β -thioxoketones, we have performed molecular orbital calculations on relevant conformeric structures.

MNDO calculations¹⁶ on hydrogen-bonded enol and enethiol tautomers of monothiomalondialdehyde **11** lend strong support to the above interpretation of the PE spectra. Calculated orbital energies and densities for the complete geometry/energy-optimized structures **11C–F** are depicted in Figure 6.

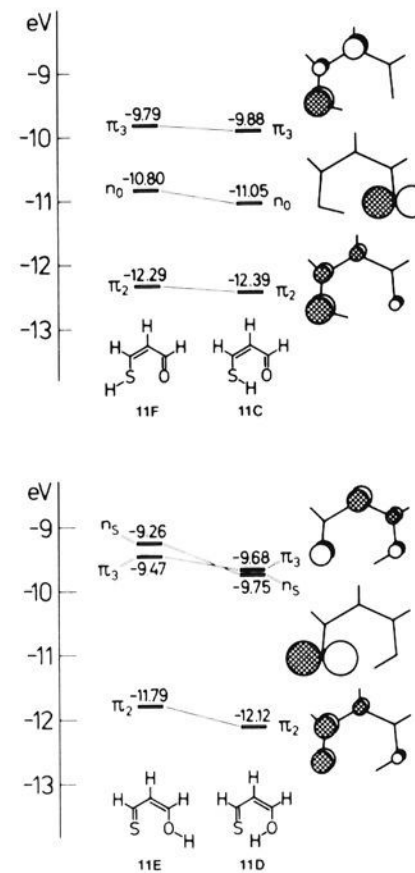


Figure 6. MNDO molecular orbital correlation diagram for the enol and enethiol forms of monothiomalondialdehyde. Numerical values refer to the calculated MO energies in eV. The circle diameters are proportional to the square of the contributing atomic orbital coefficients.

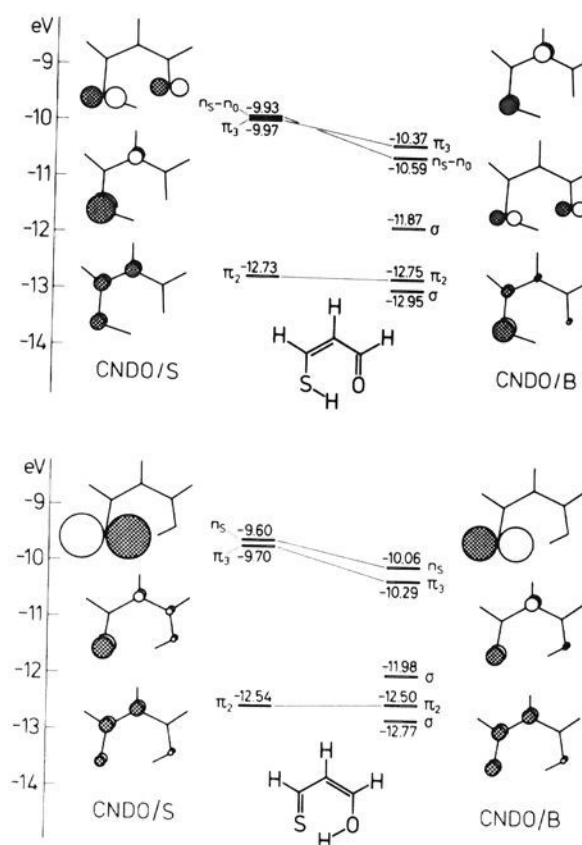


Figure 7. CNDO/S and CNDO/B molecular orbital correlation diagram for enol and enethiol forms of monothiomalondialdehyde. Numerical values refer to the calculated MO energies in eV. The circle diameters are proportional to the square of the contributing atomic orbital coefficients.

It might be of interest to compare the MNDO-calculated orbital energies and densities with results using other MO methods. In Figure 7 the orbital energies and densities of the hydrogen-chelating enol and enethiol forms of monothiomalondialdehyde (**11D** and **11C**, respectively) are displayed. The structures were obtained by a complete geometry/energy optimization using the CNDO/B procedure;¹⁴ these structures were also applied to the CNDO/S calculations.¹⁵ When MNDO results (Figure 6) are compared with those obtained by using CNDO/S and CNDO/B (Figure 7),³⁴ it is obvious that consistent results are obtained in

(30) R. Gleiter and J. Spanget-Larsen, *Top. Curr. Chem.*, **86**, 139 (1979).

(31) F. Bernardi, F. P. Colonna, G. Distefano, G. Maccagnani, and G. Spunta, *Z. Naturforsch., A*, **A33**, 468 (1974).

(32) J. H. Eland, "Photoelectron Spectroscopy", Butterworths, London, 1974. See also ref 13, pp 82–83.

(33) Electronic absorption spectroscopy of **3** in the gas phase (308 K) suggests the enol–enethiol ratio to be ca. 2:1 (L. Carlsen and F. Duus, unpublished results); see also ref 10.

(34) The CNDO/B conformational energies have been discussed in L. Carlsen and F. Duus, *J. Chem. Soc., Perkin Trans. 2*, 1080 (1980).

Table I. MNDO-Calculated Conformational Energies ($\text{kJ}\cdot\text{mol}^{-1}$) and Orbital Energies (eV) for 3-(Methylthio)-2-propenal and Nonchelated 3-Mercapto-2-propenal (11F)

	12 cis,s-cis	13 cis,s-trans	14 trans,s-trans	11F
E_{rel}	7.5	2.2	0.0	
$\epsilon(\text{HOMO})$	-9.64 (π)	-9.78 (π)	-9.75 (π)	-9.79 (π)
$\epsilon(\text{H-1})$	-10.71 (σ)	-10.76 (σ)	-10.87 (σ)	-10.80 (σ)
$\epsilon(\text{H-2})$	-11.94 (π)	-12.09 (π)	-12.08 (π)	-12.29 (π)

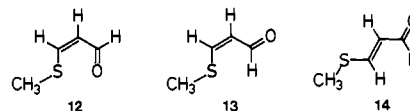
the enolic case, whereas substantial differences characterize the enethiolic case.

The three MO methods applied show that the frontier orbitals of the enol system exhibit a 2:1 pattern with the HOMO and H-1 orbitals nearly degenerate and the H-2 orbital lying significantly below these.³⁵ In accordance with experimentally determined PE data, MNDO predicts for the enethiol form a 1:1:1 frontier orbital pattern. In contrast, the CNDO/S and CNDO/B methods indicate that the HOMO and H-1 are nearly degenerate. The difference may be associated with the characteristics of the orbital placed in the plane of the molecule. MNDO suggests this orbital to possess electron density solely on the oxygen atom (n_{O}) (Figure 6) in contrast to the CNDO methods, which indicate about equal contributions from both the sulfur and the oxygen atoms ($n_{\text{S}}-n_{\text{O}}$) (Figure 7). Accordingly we suggest the MNDO method in this particular case to be superior to the CNDO methods for interpretation of the PE spectroscopic data.

The effect of hydrogen bonding on the orbital energies in the enol and enethiol forms were evaluated by optimization of the nonchelated conformers 11E and 11F (Figure 6).³⁶ By MNDO we calculate the hydrogen-bonded forms to be 17.6 and 5.0 $\text{kJ}\cdot\text{mol}^{-1}$ thermodynamically more stable than the nonhydrogen-bonded forms of the enol and enethiol systems, respectively. This is in accordance with earlier findings predicting that an intramolecular S \cdots H-O bond is stronger than the S-H \cdots O bond.³⁷ The above energy differences are smaller than those predicted by CNDO/B (enol, 22.6 $\text{kJ}\cdot\text{mol}^{-1}$; enethiol, 12.5 $\text{kJ}\cdot\text{mol}^{-1}$),³⁴ confirming that the MNDO method is less appropriate for hydrogen-bonded systems.³⁸ However, MNDO still favors the enol

form by 12.6 $\text{kJ}\cdot\text{mol}^{-1}$, in accordance with experiments.¹⁰ Thus, although some of the orbital energies are affected of hydrogen bonding, the general picture remains unchanged. The largest orbital energy differences are found for the n_{O} orbital of the enethiol system and for the n_{S} orbital of the enol system. These orbitals appear stabilized by 0.25 and 0.49 eV, respectively, on introducing the hydrogen bond, in harmony with the reported effect of hydrogen bonding on electron-donating orbitals.³⁹⁻⁴¹

In our interpretation of the PE spectra we have used the S-methyl derivative 6 as model of the enethiol form. In order to justify this choice, we have examined 3-(methylthio)-2-propenal, the corresponding S-methyl derivative on the enethiol form of monothiomalondialdehyde. The energies found by MNDO were 7.5 (12) and 2.2 $\text{kJ}\cdot\text{mol}^{-1}$ (13) relative to the trans,s-trans form



14. The orbital energies (Table I) are almost unaffected by these structural changes and appear to be close to the values calculated for the nonchelated enethiol form 11F; hence the choice of 6 as a model compound appears justified.

Conclusion

The present study has demonstrated characteristic differences between the electronic structures of tautomeric enol and enethiol forms derived from β -thioxoketones. A priori, it lends support to the established picture (ref 1, 9-11, 17, and 34) that simple β -thioxoketones do not exist as such but rather as equilibrium mixtures of rapidly interconverting intramolecularly hydrogen-bonded enol and enethiol tautomeric forms. More important, however, it calls attention to the PE spectroscopic method as a useful tool for distinguishing between the individuals of a tautomeric couple and, accordingly, for furnishing information, at least in a semiquantitative manner, about the site of a tautomeric β -thioxoketone enol-enethiol equilibrium.

Acknowledgment. We are grateful to the Danish Natural Science Research Council for purchase of a photoelectron spectrometer and to Dr. L. Henriksen (University of Copenhagen) for stimulating discussions.

(35) For simplicity HOMO, H-1, ..., refers to the highest occupied molecular orbital, the next highest occupied molecular orbital and so on.

(36) The transitions 11C \rightarrow 11F and 11D \rightarrow 11E are believed to reflect the rupture of hydrogen bonding,³⁴ although the chosen nonchelated structures 11E and 11F do not of necessity refer to actual minimum energy conformations.

(37) W. R. Snyder, H. D. Schreiber, and J. N. Spencer, *Spectrochim. Acta, Part A*, **29**, 1225 (1973); T. Schaefer, T. A. Wildman, and S. R. Salman, *J. Am. Chem. Soc.*, **102**, 107 (1980); E.-M. Sung and M. D. Harmony, *ibid.*, **99**, 5603 (1977).

(38) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **101**, 5558 (1979).

(39) R. S. Brown, *Can. J. Chem.*, **54**, 642, 1929, 3203, 3206 (1976).

(40) D. L. Ames, M. Bloch, H. Q. Porter, and D. W. Turner in "Molecular Spectroscopy", A. R. West, Ed., Heyden and Son Ltd., London, 1977, pp 410-412.

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